

**IMPACT OF A
REVISED TRIHALOMETHANE
OBJECTIVE IN ONTARIO**

JUNE 1991

TD
434
.057
147
1991



**Environment
Environnement**

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact Service Ontario Publications at copyright@ontario.ca

ISBN 0-7729-8475-1

IMPACTS OF A REVISED TRIHALOMETHANE
OBJECTIVE IN ONTARIO

Report prepared for :
Water Resources Branch
Ontario Ministry of the Environment

JUNE 1991



Cette publication technique
n'est disponible qu'en anglais.

Copyright: Queen's Printer for Ontario, 1991
This publication may be reproduced for non-commercial purposes
with appropriate attribution

PIBS 1596

IMPACTS OF A REVISED TRIHALOMETHANE OBJECTIVE IN ONTARIO

J.E. PATRICK

Ontario Ministry of Environment, Water Resources Branch,
Drinking Water Section, 1 St. Clair Avenue West, Toronto,
Ontario, M4V 1K6

ABSTRACT

Trihalomethanes (THMs) form in drinking water as a result of chlorine combining with naturally occurring humic and fulvic substances present in the raw water. Currently, chloroform, a proven animal carcinogen, is the THM of concern in terms of health effects. The Ontario Drinking Water Objective of 350 $\mu\text{g/L}$ was developed based on these health effects. Due to the presence of new toxicological data, Health & Welfare Canada has initiated a review of the current federal guideline of 350 $\mu\text{g/L}$ for total THMs. Possible adoption, in Ontario, of a lower THM guideline would have both an economic and technical impact on some water purveyors. THM data from 135 plants reveal that 25 would exceed a possible objective of 150 $\mu\text{g/L}$, while 52 would exceed a possible objective of 100 $\mu\text{g/L}$. Alternative treatment methods for THM reduction and the estimated economic impact of the changes are discussed.

KEYWORDS

Trihalomethanes; chloroform; drinking water treatment; alternative disinfection; coagulation; economics.

INTRODUCTION

The presence of trihalomethanes (THMs) in drinking water was first reported in 1974 by Rook in the Netherlands (Rook, 1974). It was found that THMs (chloroform, bromodichloromethane, chlorodibromomethane, and bromoform) were formed during the chlorination stage of drinking water treatment. Studies suggest that chloroform is a probable carcinogen (H&WC, 1978). The other THMs are presumed to have long term health effects also.

The Ontario Drinking Water Objective for THMs, of 350 $\mu\text{g/L}$, is now under review. A revised objective may be set at 150 $\mu\text{g/L}$ or lower.

A lower objective for acceptable levels of THMs in drinking water will have a technological and economic impact on water treatment in Ontario. Maintaining the microbiological integrity of the treated water, as changes are made to achieve reduced THM levels, is an essential constraint. This paper will give consideration to the formation of THMs, the current and possible revised THM limit, THM levels in Ontario, approaches for controlling THMs, and the economic impact of implementing

the revised objective.

Several benefits would result from a lowered THM objective. First, a lower limit would commit the water industry to more stringent control of THMs. The Drinking Water Surveillance Program for Ontario shows THMs to be the only significant contaminants that regularly occur in drinking water from surface water sources. Secondly, tightening THM control would probably ensure the control of other chlorinated and organic by-products in the finished water. Thirdly, a lower THM objective may improve the overall quality of drinking water, as many water purveyors would be required to review and improve control of their treatment processes (Vajdic, 1989a).

IMPORTANCE OF DISINFECTION

The sole purpose of disinfecting drinking water is to eliminate pathogenic organisms and prevent the spread of waterborne disease.

There are many diseases that are known to be transmitted by water. Historically, the virulent outbreaks of typhoid fever and cholera led to the practice of chlorinating,

drinking water supplies. Hundreds of thousands of deaths and illness have been attributed to these, and other waterborne diseases (White, 1986).

Since the turn of the century, the conscientious use of chlorine, for drinking water disinfection, has diminished the threat of major outbreaks of waterborne disease. Now, changes to disinfection practice should be considered very cautiously. The perceived risk of long-term health effects from low levels of chlorinated by-products should be weighed against the actual risk of bacterial contamination (Orme, 1989). Maintaining safe and reliable disinfection barriers must remain a primary treatment goal.

FORMATION OF TRIHALOMETHANES

THMs belong to a group of organic compounds that contain one carbon atom, one hydrogen atom, and three halogen atoms. These compounds are named as derivatives of methane (CH_4). A generic structural formula for THMs is CHX_3 , where X could be any halogen such as chlorine, bromine, iodine, fluorine, or a combination of halogens (H&WC, 1978).

The formation of THMs results when free chlorine reacts with natural organic matter (NOM) in water. Figure 1, illustrates the components of THM formation.

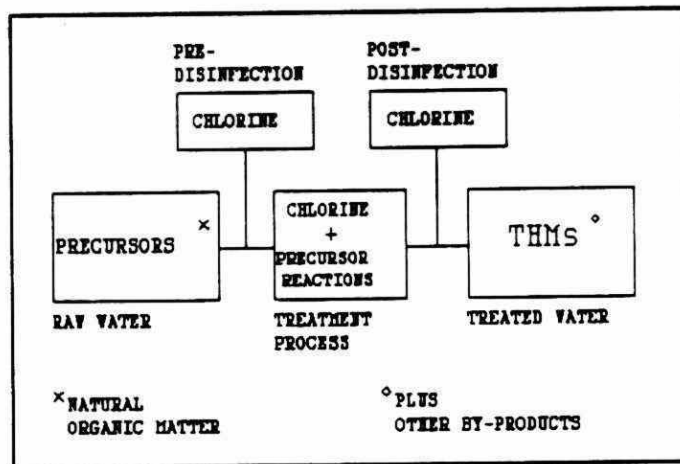


Fig. 1. Trihalomethane formation

NOM is also known as precursor material. Humic substances, such as humic and fulvic acids, and algae, are the principal precursors of THMs. They represent a major portion of the total organic content (TOC) of the raw water (Singer, 1989). Although precursors are not commonly measured directly, parameters such as TOC, colour, and THMs, do indicate the presence of THM precursor material.

There is a potential for the formation of ten different THM compounds. The THMs produced in chlorinated drinking water are, however, dominated by four species: chloroform, bromodichloromethane, chlorodibromomethane, and bromoform. The structural formula for each of these compounds is illustrated in Figure 2. Chloroform is the THM most commonly found, and at the highest levels, in Ontario drinking water.

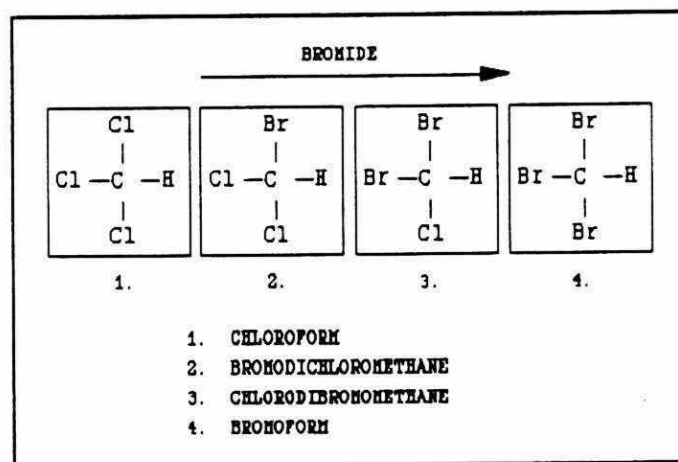


Fig. 2. Trihalomethanes in drinking water

Brominated THMs form when bromide is present in the source water, or as a trace impurity in the chlorine used for disinfection. The distribution of the four THMs depends on how much bromide is present. Elevated bromide

levels will cause a shift in the distribution toward the bromide-containing species (Cooper et al., 1985).

Usually, surface waters contain significant levels of NOM and therefore produce more THMs than ground waters. In Ontario, river sources generally have the highest concentrations of NOM and have the potential to produce the highest levels of THMs.

Factors that affect THM formation are temperature, contact time, pH, and the concentration of precursors, free chlorine, and bromide. THM formation is not instantaneous. The reaction may continue for several days, as long as free chlorine and precursors are present in the water. Levels are expected to be highest in situations of seasonal variation; that is, when water temperatures or precursor concentrations are elevated. In general, the rate and extent of THM formation increases as the factor levels increase (Singer, 1989).

TRIHALOMETHANE GUIDELINE/OBJECTIVE

The Canadian guideline for THMs in drinking water is 350 $\mu\text{g/L}$, expressed as a maximum acceptable concentration not to be exceeded. Based on new toxicological information, this guideline level is under review. In order to understand the review process, guideline development in Canada is discussed (Vajdic, 1989b).

The Canadian guideline levels for drinking water quality are set by a Federal/Provincial Subcommittee on Drinking Water. The Subcommittee is made up of representatives from Health and Welfare Canada (H&WC), each of the provinces and territories, and Environment Canada. Factors such as health aspects, treatment technology capabilities, and economic implications are considered by the Federal/Provincial group, before a limit for a proposed guideline is set.

Substances selected for guideline development or review undergo a health risk assessment process. The physical and chemical properties of a substance, and its health effects, are reviewed by H&WC. The results of both epidemiological and toxicological studies are used to

classify the carcinogenic potential of the substance. For carcinogenic substances, cancer risk is estimated by applying a mathematical extrapolation model to the most appropriate toxicological data. The extrapolation model used by H&WC, to determine the cancer risk for THMs, the robust linear model, is now known as the model free approach.

Cancer risk is estimated for a 70-kg person who ingests 1.5 litres of water daily, over a lifetime. When establishing limits for drinking water, the level of cancer risk commonly used is 1 in 100,000 (10^{-5}). If, however, exposure to the substance from other sources is significant, the level of lifetime cancer risk from drinking water should be 1 in 1,000,000 (10^{-6}) or less.

Chloroform is the predominant THM in drinking water and the most widely studied for health effects. Exposure to chloroform at doses of 60 mg/kg or more, has produced effects, ranging from mild serum changes to irreversible damage, to the liver and kidney in rats, mice, and dogs (Orme, 1990).

Toxicity data indicates that chloroform administered by gavage in corn oil produced an increased incidence of kidney tumours in male rats and liver tumours in male and female mice. A more recent study reported kidney tumours in male rats exposed to chloroform in drinking water (Orme, 1990). Chloroform, therefore, is considered an animal carcinogen. Evidence of carcinogenicity in humans is inconclusive (Orme, 1990; Ram et al., 1990).

Although the other THMs have not been studied for toxicity to the same extent as chloroform, their effects are similar. Brominated THMs decrease immune function in mice and also produce changes to the liver and kidney (Orme, 1990).

The health risk assessment process, using new information on chloroform toxicity, indicates that a cancer risk of 10^{-6} may be associated with a THM level below 150 $\mu\text{g/L}$, expressed as an annual average.

Economic consequences are also considered during the proposal or revision of national drinking water guidelines. The impact on each Canadian jurisdiction is

taken into account. In Ontario, several steps were followed in order to determine the effect of a lowered THM objective.

First, using available data, a profile of occurrence and levels of THMs at selected municipal water supplies across the province was established. The information, based on yearly averages, was organized to categorize the water supplies as to the levels of THMs produced, for example, those producing THMs greater than 150 $\mu\text{g/L}$, 100 $\mu\text{g/L}$, 50 $\mu\text{g/L}$, or 10 $\mu\text{g/L}$. Secondly, treatment technologies for removing or reducing THMs were investigated. Finally, the cost (per million gallons of treated water) for each technology was estimated. The estimates were then applied to the selected water supplies and an overall cost for the province was calculated.

The process of guideline setting is dynamic, and the limits may change as new information becomes available. In conclusion, health effects assessment, the availability of treatment technologies, and cost, are all part of guideline development for drinking water. Ontario

usually adopts the Canadian guidelines as the Ontario Drinking Water Objectives.

TRIHALOMETHANES IN ONTARIO DRINKING WATER

A profile of the occurrence and levels of THMs in Ontario municipal water supplies was established from two sources of data. Ministry of the Environment programs supplied both sets of information.

The results of one program, a THM survey of 135 municipal water supplies across the province, were published in 1985 (Martin et al., 1985). The survey was conducted during the period from 1977 to 1982, and was designed to accommodate monthly sampling. The number of samples taken at each site varied depending on the number of years, and the degree of participation, in the program.

Results from the ongoing Drinking Water Surveillance Program (DWSP) were also used to estimate the extent of THM production at 60 water supplies. Data for these supplies was based on monthly sampling in 1988 and 1989.

There was an overlap of 53 locations between the two

programs. A composite of the available THM data provided information for a total of 142 locations.

The THM survey showed that 25, or 18.5 percent, of the 135 water supplies tested would probably exceed a THM guideline of 150 $\mu\text{g/L}$ as an annual average, and that 52, or 38.5 percent, would probably exceed a guideline of 100 $\mu\text{g/L}$.

The DWSP data indicated that two, or 3.3 percent, of the 60 plants currently on the program would exceed a guideline of 150 $\mu\text{g/L}$ as an annual average, and that 11, or 18.3 percent, would exceed a guideline of 100 $\mu\text{g/L}$.

The difference in the predictions derived from the two sets of data can be explained. The majority of water supplies that are currently on DWSP use the Great Lakes as a source of water. Since the Great Lakes water is generally low in precursor material, the treated water THM levels tend to be low. The THM survey covered a wider variety of water supplies in terms of the water source used and the population served. The results of this latter program are considered to be more representative

of THM levels in Ontario municipal water supplies.

Figure 3, includes three types of information, from both studies, organized into categories of THM production: greater than 150 $\mu\text{g/L}$, 150-100 $\mu\text{g/L}$, 100-50 $\mu\text{g/L}$, 50-10 $\mu\text{g/L}$, and less than 10 $\mu\text{g/L}$. The first three items show the number of municipal water supplies, using river, lake, and groundwater sources, producing THM levels within each category. The number of plants having a system capacity of less than 1 million gallon per day (MGD), that produce THMs at concentrations within the various ranges, are shown as well.

SOURCE	THM CATEGORY ($\mu\text{g/L}$)				
	>150	150-100	100-50	50-10	<10
RIVER SOURCE	17	14	8	9	0
LAKE SOURCE	7	13	16	36	0
GROUNDWATER	1	0	1	11	11
TOTAL LOCATIONS	25	27	23	56	11
PLANT CAPACITY < 1 MGD	11	13	3	7	6

Fig. 3. THMs in Ontario drinking water

The chart indicates that 24, or 46 percent, of the 52

plants that produce THMs at levels greater than 100 $\mu\text{g/L}$ have a system capacity of less than 1 MGD, whereas most of the 90 plants that produce levels of THMs less than 100 $\mu\text{g/L}$, have a capacity greater than 1 MGD.

Figure 4, shows the number of water supplies, for which THM data is available, that would probably produce THM concentrations exceeding suggested THM limits.

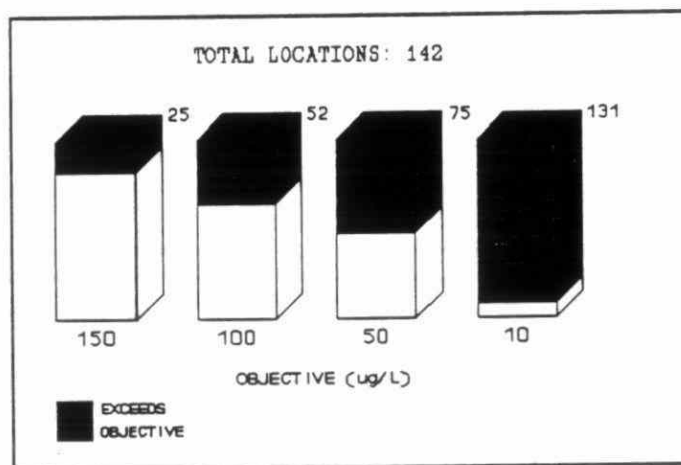


Fig. 4. Number of locations exceeding potential THM objectives

The two studies supply information for approximately 30% of the 486 municipal water supplies in Ontario.

APPROACHES FOR CONTROLLING TRIHALOMETHANES

The three main treatment approaches for controlling the levels of THMs in drinking water are (Symons et al., 1981):

1. Treatment to remove THM precursors
2. Use of alternate disinfectants
3. Treatment to remove THMs after formation

There are advantages and disadvantages to each of these approaches, some of which are discussed below.

An important advantage of removing THM precursors or removing THMs after formation, is that plants using free chlorine could continue to do so. Chlorination is still the disinfection method of choice in Ontario and utilities are familiar with its application.

Removal of THM precursors would result in an improved water quality and fewer disinfection by-products of all types. Lower concentrations of precursor material would also decrease the disinfectant demand. Finally, the transport of organic and inorganic impurities, through

the treatment facility and into the finished water, would be expected to decrease.

A major disadvantage of removing THMs after formation, is the lack of precursor removal. Precursors remaining in the treated water will continue to react with a free chlorine residual; therefore, THM levels in the distribution system may increase. The potential also exists for the formation of other disinfection by-products, such as those formed by oxidation, that may not be removed by THM removal processes.

A distinct advantage of using alternative disinfection, as an approach to controlling THMs, is that none of the alternative disinfectants react with humic substances, or other organic matter in the water, to produce significant concentrations of THMs. It should be noted, however, that the alternative disinfectants and resulting by-products may themselves be toxic and produce health effects that are not fully understood.

Of primary importance when choosing an alternative to chlorine is the disinfecting power of the disinfectant.

The role of disinfection in the reliable production of drinking water is well established. Chlorination is the predominant method of disinfection because of its potency and range of effectiveness as a germicide.

There are other factors that warrant the acceptance of chlorine as a disinfectant. Chlorine produces a lasting residual which prevents bacterial deterioration and aftergrowths in the distribution system. In addition, with respect to plant operation, chlorine can be easily applied, monitored, and controlled. Finally, chlorination is a cost effective method of disinfection (Vajdic, 1982). For all these reasons, a replacement for chlorine should be evaluated very carefully.

The following treatment methods can be used to control the level of THMs in drinking water:

- coagulation
- granular activated carbon
- ozone disinfection
- chlorine dioxide disinfection
- chloramine disinfection
- air-stripping

Coagulation

Coagulation, using coagulants such as aluminum sulphate (alum), or ferric chloride, may reduce the THM precursor content of a water supply by 50 to 75 percent. When used for precursor removal, however, coagulation must precede chlorination in order to be effective.

The effectiveness of coagulation depends greatly on the ability to optimize the chemical process. Two major factors influencing the success of coagulation are the coagulant dose and pH. Experience indicates that the optimum dose of either alum or ferric chloride, will yield the lowest residual of aluminum or iron in the finished water. Doses higher or lower than optimum will result in elevated levels of coagulant residual. Optimum coagulation, as measured by residual aluminum or iron, means that a completed chemical reaction has occurred between the coagulant and the water.

The raw water pH may also affect the efficiency of coagulation. As aluminum is soluble in water at a pH less than 4 and greater than 8, the recommended pH range for coagulation with alum is 5 to 7. Alum can be effective

on most waters within this range. Ferric chloride can be used up to a pH of 11.

When alum is added to water having a pH near one of these limits, a portion of aluminum will remain in solution. The chemical reaction between the alum and the water will be incomplete and the efficiency of coagulation will decrease. The decrease in efficiency is marked by elevated residual aluminum in the treated water. In order to achieve optimum coagulation, pH adjustment to the raw water may be necessary.

Temperature also affects coagulation reactions. Low temperatures will slow the development of the chemical reaction. In cold water, longer reaction times may be necessary in order to obtain good precursor removals.

The greatest advantage of using chemically-assisted coagulation, for controlling THMs, is that most surface water plants already use this treatment process. Optimum coagulation, for maximum precursor removal, may be achieved at most plants with relatively minor modifications and minimal cost.

Granular Activated Carbon

For THM precursor removal, granular activated carbon (GAC) filtration is most effective after conventional treatment (post-filter adsorption) but before the addition of chlorine. Coagulation prior to GAC filtration extends the life of the carbon bed and improves TOC removal. Coagulation should be optimized in order to remove the largest amount of high molecular weight precursor material, and thereby reduce the organic load on the carbon bed. The installation of this treatment technique depends on the design configuration of the water treatment plant.

The effectiveness of GAC for precursor removal depends on a number of factors such as the level of TOC in the raw water, the molecular size and distribution of the precursor materials, the pore size distribution of the GAC, and the empty bed contact time (EBCT).

Different source waters can be expected to have a wide variety of NOMs that will compete for adsorption sites on the carbon; some precursors may be removed, whereas others may not. High molecular weight species of

precursor material will be excluded from GAC pores, if the pores are too small. The adsorption mechanism will be restricted to the carbon surface, making precursor removal a slow process requiring relatively long EBCTs. Both the rate of adsorption and the adsorption capacity are influenced by the molecular weight and size of the precursor material relative to the pore size of the carbon (Singer, 1989).

Not all types of GAC have the same adsorptive capacity, and so one type of carbon may not perform equally well on different source waters. GAC must, therefore, be evaluated on-site (by pilot plant studies) for its ability to remove organic impurities (Vajdic, 1983).

THM removal, after formation, can be accomplished using GAC. Carbon filtration is, however, less efficient for the removal of THMs than for precursors, and is considered unsuitable for complete THM removal over a long period of time (Kruithof, 1986). GAC is an expensive method of THM control due to the relatively long EBCTs and the frequency of reactivation required (Singer, 1989).

Ozone Disinfection

Ozone has been used extensively in Europe as a disinfectant and oxidant in drinking water treatment, and is rapidly gaining acceptance in North America (Grasso et al., 1989; Larocque, 1990). There are over sixty plants in Canada using ozonation for potable water treatment. In Ontario, the first ozone installation was completed in 1988, at the Atikokan Water Treatment Plant (Larocque, 1990).

Disinfection. Ozone is one of the most powerful oxidants available, having at least twice the oxidizing power of chlorine as a disinfectant (Glaze et al., 1989). Ozone does not, however, maintain a residual and should not be relied upon as the total solution for disinfection.

Health Effects. Knowledge of the health effects of ozone and ozonation by-products in drinking water is limited. Studies indicate that the degree of ozone induced mutagenic activity, in water, appears to be dependent on process conditions such as ozone dosage and raw water characteristics (Singer, 1990). Major substances formed through direct ozone reactions include aldehydes such as formaldehyde, carboxylic acids, and ketones (Glaze et

al., 1989; Janssens, 1990). There are many by-products of ozonation, especially those resulting from radical reactions, that have not yet been identified (Orme et al., 1990; Janssens, 1990). Of the known reaction products, formaldehyde has received the most thorough toxicological investigation. Exposure to formaldehyde through inhalation has produced nasal carcinomas in mice and rats; exposure through ingestion showed no ill effects in animals (Janssens, 1990).

THM Control. When used prior to chlorination, ozone oxidizes organic matter which may decrease the levels of THMs in the treated water. In some cases, however, ozone may produce THM precursors from non-precursor organic material, thereby enhancing THM formation (Glaze, 1986).

Uses. Ozone is used mainly as an oxidant for taste and odour control, decolorization, and removal of iron and manganese. When used as a pre-oxidant, ozone can act as a microflocculant (coagulant aid) on some waters (Reckhow et al., 1986). As a microflocculant, ozone improves the effectiveness of chemical flocculants, allows higher filtering rates and longer filter runs, and saves on treatment chemical costs (Prendiville, 1985; LePage, 1985).

Disadvantages. Under certain conditions, ozone may have a detrimental effect on the treated water quality. When ozone oxidizes natural organics in the raw water, a regrowth of microorganisms in the plant or distribution system may occur (Glaze et al., 1989). For this reason ozonation should not be the last step of the treatment train. Filtration and disinfection, to maintain a residual in the distribution system, should follow.

Chlorine Dioxide Disinfection

Chlorine dioxide has been used as a disinfectant and oxidant in drinking water treatment since 1944 (Aieta, 1986). Several thousand utilities in Europe, and several hundred utilities in North America use chlorine dioxide.

Disinfection. Theoretically, the disinfection efficiency of chlorine dioxide is equal to or superior to that of free chlorine, and is surpassed only by ozone (Aieta, 1986). It has nearly 2.5 times the oxidizing power of chlorine (Orme, 1990) and stronger virucidal properties (Kruithof, 1986). In water treatment, however, this full oxidizing potential is not realized. Chlorine dioxide is capable of maintaining a stable residual in the

distribution system.

Health Effects. The major by-products of chlorine dioxide generation and use are inorganic chlorite and chlorate. The acute health effects of chlorine dioxide and its by-products appear to be significant, and reason for concern. Studies indicate that exposure to chlorite, chlorine dioxide and chlorate, causes haemolytic oxidative stress (methaemoglobin, haemolytic anaemia) in rats (Bull, 1982; Condie, 1986). Chlorine dioxide has also been found to produce changes in serum thyroxine levels (hypothyroid activity) in monkeys and developing rats (Harrington et al., 1986; Orme et al., 1985). This effect appears to be unique to chlorine dioxide and does not occur following exposure to chlorite or chlorate (Bercz et al., 1982). Only limited information is available regarding the reaction products that are produced by chlorine dioxide. More information is needed to determine chronic health problems (Kruithof, 1986).

THM Control. THMs can be reduced by the use of chlorine dioxide as a preoxidant and primary disinfectant, followed by free chlorine (Aieta, 1986).

Uses. As an oxidant, chlorine dioxide reduces colour, iron and manganese, and controls taste and odour (primarily problems associated with phenols and algae).

Typical doses of chlorine dioxide, in the United States, range from 0.1 to 5.0 mg/L (Aieta, 1986). In Europe, the levels of chlorine dioxide used are lower, 0.02 to 0.1 mg/L (Kruithof, 1986). Many European water treatment facilities use granular activated carbon pre-treatment to remove organic matter. This additional process would decrease the disinfection demand so lower doses could be used.

Disadvantages. Due to its unstable, explosive nature, chlorine dioxide must be generated on site. Chlorine dioxide generators, if they are not performing properly, may release potentially harmful by-products, such as chlorite and chlorate, into the water. Generator technology and optimization is a major consideration, and sophisticated chemical testing is routinely required. Careful generation is needed to maintain low concentrations of chlorine and chlorate in the chlorine dioxide effluent (Lauer et al., 1986).

There seems to be more problems associated with the use of chlorine dioxide than with the other alternative disinfectants (Bull, 1982). Many countries have placed limitations on the use of chlorine dioxide as a disinfectant. For example, the maximum addition rate in Germany and Belgium is 0.10 and 0.25 mg/L respectively. The use of chlorine dioxide is banned in Norway (Kruithof, 1986). The U.S. Environmental Protection Agency recommend the combined concentrations of chlorine dioxide, chlorite, and chlorate, in drinking water be limited to 1.0 mg/L because of health effects (Gordon et al., 1990).

Chloramine Disinfection

Chloramine (combined chlorine) has had limited use as a disinfectant in drinking water treatment in North America since the 1920s.

Disinfection. Chloramines (monochloramine, dichloramine, and trichloramine) form when both chlorine and ammonia are present in water. Monochloramine is a weak disinfectant, but is considered to be more stable in

water than chlorine (Kruithof, 1986). Higher chloramine concentrations and longer contact times are required to equal the effectiveness of free chlorine.

Chloramine is not generally recommended for primary disinfection because of its lack of germicidal power. Its main use is for secondary disinfection. Chloramine has, however, been used successfully as a disinfectant on high quality water with low concentrations of bacteria (Dice, 1985).

Health Effects. Little information has been collected regarding the health effects of chloramines. Most research has been directed toward the oxidative effects on blood. The available information indicates that chloramines may be mutagenic in bacteria and are being tested for carcinogenicity in animals (Kreft et al., 1985). In addition, chloramine may produce haemolytic anaemia in kidney dialysis patients (Kreft et al., 1985); chloramine and ammonia are known to be toxic to aquarium fish at microgram-per-litre levels (Kreft et al., 1985).

THM Control. Chloramine disinfection can be used to impede the formation of THMs (Sayre, 1985).

Uses. Chloramine is applied at some water treatment plants, following post-chlorination, to produce a long lasting residual in the distribution system. It has been used for this purpose in Toronto for over ten years. Chloramination is useful for large distribution systems because of its residual persistence (Kreft et al., 1985).

Disadvantages. There are some potential problems associated with the use of chloramine in drinking water treatment. For example, under certain conditions taste and odours can be produced. If the chlorine to ammonia-nitrogen ratio is not controlled to produce monochloramine as the predominate species, dichloramine and/or trichloramine could form. Both of these compounds inherently have offensive odours and are potential sources of taste and odours in distribution systems (Kreft et al., 1985). The order of addition of the chlorine and ammonia, and the mixing conditions, also affect the formation of the various chloramines.

Another concern is the loss of a chloramine residual. The inorganic reaction of chlorine with ammonia-nitrogen, in

water, produces what is known as the breakpoint phenomenon (White, 1986). Ideally, a chlorine to ammonia-nitrogen weight ratio of up to 5:1 converts all the free chlorine to monochloramine, at pH 7 to 8 (White, 1986). As the ratio increases, dichloramine and other reaction products form; the theoretical breakpoint occurs at a chlorine to ammonia-nitrogen ratio of 7.6:1 by weight (Barrett, 1985). After this point, free chlorine and nuisance residuals will be present, as no total ammonia-nitrogen remains (Barrett, 1985; White, 1986).

The mixing of water containing chloramine with water containing free chlorine could cause a breakpoint reaction, resulting in a loss of a chloramine residual (Dice, 1985; Kreft et al., 1985). Since no disinfection residual exists at breakpoint, the condition is undesirable (Barrett, 1985).

Air-Stripping

THMs can be removed from water through contact with air, in packed towers or in diffused or mechanical aeration systems (Roberts, Levy, 1985). The degree of removal depends on the Henry's Law constant for the different THM

species. The order of stripping is: chloroform > bromodichloromethane > chlorodibromomethane > bromoform (Singer, 1989).

In theory, the countercurrent packed tower is the most effective air-stripping technology for THM removal. Contactor design is very critical to the efficiency of the method. The ideal tower design uses the minimum air-water ratio that will produce complete substance removal (Symons et al., 1981).

There are disadvantages to using air-stripping to control THMs. The volatile species will be removed but the less volatile ones may not (Singer, 1989). Soluble disinfection by-products will not be removed at all. Also, when free chlorine is used as the final disinfectant, THMs will continue to form in the distribution system. Finally, air-stripping does not destroy the contaminants it removes from water, but merely transfers them from one medium (water) to another (air).

ECONOMIC IMPACT

Six treatment methods for controlling THMs in drinking water were reviewed. Five of these methods, activated carbon, ozonation, chlorine dioxide disinfection, chloramination, and air stripping, will have significant economic implications for the province.

Costs were calculated for each treatment method. The estimate for GAC treatment was derived from cost data published by the U.S. Environmental Protection Agency in 1989 (Adams et al., 1989). Estimates for all the other treatment methods were obtained from a cost analysis published by the American Water Works Association in 1982 (Symons et al., 1981). The original unit costs, provided by these sources, were adjusted for inflation and the U.S./Canadian dollar differential.

The original numbers were based on a water plant capacity unit of MGD. Since Ontario uses million Imperial gallons per day (MIGD), the plant capacity factor was also adjusted before calculating the treatment costs.

Total treatment costs include amortized capital cost,

plus operation and maintenance expenses. All calculations were based on a system capacity of 10 MGD. This capacity was chosen for two reasons. First, it was the only cost data accessible, for all methodologies, from the available information. Secondly, a constant number allows a more accurate comparison of the costs. The average design capacity for Ontario water treatment plants is 5.6 MGD.

The removal processes, granular activated carbon and air stripping, are the most expensive methods for THM control. Figure 5, gives a breakdown of the total treatment cost for these processes.

TREATMENT	COST (\$/MG of Treated Water)		
	TOTAL	CAPITAL	OPERATION
GRANULAR ACTIVATED CARBON	706	565	141
AIR STRIPPING	94	66	28

Fig. 5. Cost analysis for removal processes

GAC filtration is a very expensive method of THM control. The total cost, per million gallons of treated water, is estimated to be \$706 (\$2.6 million annually), for a 10 MGD plant. Capital expenditure constitutes a major portion (70-90%) of the total cost for GAC installation and use.

GAC treatment costs vary depending on the plant capacity; large systems are more economical than smaller systems. A gradual increase of unit cost exists for system sizes from 200 MGD to 1 MGD. The costs increase sharply for systems smaller than 1 MGD. Total costs, per million gallons of treated water, range from \$356 for a 200 MGD system to \$2,480 for a 0.1 MGD system.

On-site reactivation is a major portion of the cost of GAC treatment. In some cases it may account for more than 50 percent of the total amount.

The figures presented here may overestimate the true cost of precursor removal by GAC. Costs were based on a GAC bed life of 60 days which may reflect worst case conditions. GAC has been found to effectively remove precursors for up to six months on some waters.

The total cost of air-stripping, per million gallons of treated water, is estimated to be \$94 (\$0.34 million annually), for a 10 MGD plant. Capital costs account for about 70 percent of this amount.

The cost analysis for the removal processes is based on the assumptions described in Figure 6.

GRANULAR ACTIVATED CARBON		AIR STRIPPING	
SYSTEM CAPACITY	10 MGD	SYSTEM CAPACITY	10 MGD
GAC COST	\$1.14 /lb	TOWER HEIGHT	20 ft
EBCT	15 min	AIR SUPPLY	52.25 SCF/FT ³
BED LIFE	60 days	AIR/WATER RATIO	100:1
REACTIVATION	OFF-SITE X		

X MULTIEARTH

Fig. 6. Cost assumptions for removal processes

Disinfection using alternate disinfectants, appears to be the most cost effective method of reducing THMs in drinking water. Figure 7, displays a breakdown of the total treatment cost of ozone, chlorine dioxide, and chloramine. A cost estimate for chlorine was included for comparison.

TREATMENT	COST (\$/MG of Treated Water)		
	TOTAL	CAPITAL	OPERATION
CHLORINE	15	4	11
OZONE	42	29	13
CHLORINE DIOXIDE	42	6	36
CHLORAMINE	46	12	34

Fig. 7. Cost analysis for alternative disinfectants

Ozonation is almost three times the cost of chlorination. The total cost of treatment using ozone is estimated to be \$42 per million gallons of finished water. Capital expenditure accounts for almost 70 percent of this amount.

The total cost of chlorine dioxide is estimated to be \$42 per million gallons of treated water. Although this estimate appears to equal the cost of ozonation, the distribution of the expenses differ. Operation and maintenance represents over 85 percent of the total cost of chlorine dioxide disinfection.

For new plants, the cost of chloramination (chlorine and

ammonia) is slightly higher than that of the other disinfectants. For every one million gallons of treated water, the total cost is estimated to be \$46. About 75 percent of this amount should be allotted for operation and maintenance. Estimates will be lower at existing plants where chlorine equipment is already in use and only ammonia installation is required. The use of chloramine for primary disinfection may require comprehensive and costly monitoring and distribution system maintenance programs (Dice, 1985).

The cost analysis for alternative disinfection is based on the assumptions described below, in Figure 8.

TREATMENT	DOSE ×	COSTS	SYSTEM CAPACITY	CONTACT TIME
	mg/L	\$/lb	MGD	min
CHLORINE	2	1.39	10	20
OZONE	1	-	10	10
CHLORINE DIOXIDE	1	1.39 9.35 ○	10	20
CHLORAMINE	3	1.39 0.93 ◇	10	20

× EQUIVALENT DOSES ○ SODIUM CHLORITE ◇ AMMONIA

Fig. 8. Cost assumptions for alternative disinfectants

The expense of operating municipal water treatment plants in Ontario, for THM control, is represented in Figure 9. The table shows the annual total treatment cost of each treatment method, for water supplies that would produce THM concentrations exceeding various potential THM objectives.

TREATMENT METHOD	POTENTIAL OBJECTIVE (UG/L)			
	150	100	50	10
CHLORINE	0.6	1.8	2.4	11.0
OZONE	1.8	5.1	6.8	30.8
CHLORINE DIOXIDE	1.8	5.1	6.8	30.8
CHLORAMINE	1.9	5.6	7.4	33.7
GAC	24.3	60.4	86.6	293.7
AIR STRIPPING	3.9	11.4	15.1	68.8

Fig. 9. Annual total treatment costs (millions of dollars)

The available THM data supplied information on 142 municipal water supplies. This accounts for 29 percent of 486 municipal water supplies in Ontario. The treatment costs in Figure 9, therefore, represent only one-third of the total cost to the province.

SUMMARY

The current objective for THMs in drinking water, 350 $\mu\text{g/L}$, is under review. A revised objective will result in changes to disinfection practices at many municipal water treatment plants in Ontario. Chlorine disinfection has been used successfully for almost a century, and changes should be considered very cautiously. Safe and reliable disinfection barriers must be maintained.

A lowered THM objective will have a significant technological and economic impact on water treatment in the province. An objective of 150 $\mu\text{g/L}$ will necessitate changes to treatment processes at 25 water supplies. The cost of new technologies to lower THM levels at these plants was estimated to be in the range of \$1.8 to \$24.3 million annually, depending on the treatment methods used.

Fifty-two water plants will require treatment changes to accommodate a THM objective of 100 $\mu\text{g/L}$. The economic impact is considerable; the cost of the technological changes was calculated to be \$5.1 to \$60.4 million annually.

The recommended approach for THM control is optimum coagulation, where it can be used prior to chlorination. Coagulants such as alum or ferric chloride will remove precursor material, resulting in improved water quality and decreased disinfectant demand. Optimum coagulation, for a given source water, is determined mainly by measuring the level of residual coagulant (aluminum or iron) in the treated water. The lowest residual signifies an optimum chemical reaction — this hypothesis indicates the need for continuous on-site monitoring of aluminum or iron, where alum or ferric chloride is used, for process control.

As most surface water treatment plants already use chemically-assisted coagulation, optimum coagulation may be achieved with minor modifications and minimal cost. Optimizing the chemical treatment process should be the first step when attempting to reach a desired THM goal. Water plant optimization, as sound treatment practice, should be carried out routinely by all plants whether or not THMs are a concern.

As all raw source waters are different, the applicability of the other treatments must be fully assessed on a case-by-case basis. More than one treatment method may be necessary to reduce THMs in some waters, depending on the chemical make-up of the source. Disinfection using alternative disinfectants appears to be the most cost effective approach of the remaining methods.

The arrival of new water treatment technologies brings a need for expertise. Implementation of treatment changes should include, and be followed by, training and development for plant operations personnel. Unfortunately, many of the plants that will probably require substantial changes are small (less than 1 MGD), and do not have the resources to dedicate staff to the job of water treatment. It is strongly advised that expertise and support be available to plants contemplating treatment upgrades.

THMs are the first chemical compounds to make an impact on drinking water treatment in Ontario. Until now, the water produced by municipal supplies has been able to meet the quality standards set out in the Ontario

Drinking Water Objectives. As objectives change, however, and as analytical techniques become more sophisticated, this situation could reoccur for any number of contaminants.

REFERENCES

- Adams, J.Q., R.M. Clark and R.J. Miltner (1989). Controlling Organics with GAC: A Cost and Performance Analysis. *JAWWA*, 81:4 132-140.
- Aieta, M.E. and Berg, J.D. (1986). A Review of Chlorine Dioxide in Drinking Water Treatment. *JAWWA*, 78:6, 62-72.
- Barrett, S.E., M.K. Davis and M.J. McGuire (1985). Blending Chloraminated and Chlorinated Waters. *JAWWA*, 77:1, 50-61.
- Bercz, J.P., L. Jones, L. Garner, D. Murray, D.A. Ludwig and J. Boston (1982). Subchronic Toxicity of Chlorine Dioxide and Related Compounds in Drinking Water in the Nonhuman Primate. *Environ. Health Perspect.* 46, 47-55.
- Bull, R.J. (1982). Health Effects of Drinking Water Disinfectants and Disinfectant By-products. *Environ. Sci. Technol.*, 16:10, 554A-559A.
- Condie, L.W. (1986). Toxicological Problems Associated With Chlorine Dioxide. *JAWWA*, 78:6, 73-78.
- Cooper, W.J., R.G. Zitka, and M.S. Steinhauer (1985). Bromide-oxidant Interactions and THM Formation, A Literature Review. *JAWWA*, 77:4, 116-121.
- Dice, J.C. (1985). Denver's Seven Decades of Experience With Chloramination. *JAWWA*, 77:1, 34-37.
- Glaze, W.H. (1986). Chemistry of Ozone, By-products and Their Health. In: *AWWA Seminar Proceedings. Ozonation: Recent Advances and Research Needs*. Annual Conference. June 22, 1986. Denver, Colorado. American Water Works Association, Denver, CO. pp. 1-15.
- Glaze, W.H., M. Koga, D. Cancilla and K. Wang (1989). Ozone as a Disinfectant and Oxidant in Water Treatment. *Disinfection By-Products, Current Perspectives*. American Water Works Association, Denver, CO. pp. 255-270.

- Gordon, G., B. Sloodmaekers, S. Tachiyashiki and D.W. Wood (III) (1990). Minimizing Chlorite Ion and Chlorate Ion in Water Treated With Chlorine Dioxide. *JAWWA*, 82:4, 160-165.
- Grasso, D., W.J. Weber Jr. and J.A. DeKam (1989). Effects of Preoxidation with Ozone on Water Quality: A Case Study. *JAWWA*, 81:6, 85-92
- Harrington, R.M., H.G. Shertzer and J.P. Bercz (1986). Effects of Chlorine Dioxide on Thyroid Function in the African Green Monkey and the Rat. *J. Toxicol. Environ. Health*. 19:2, 235-242.
- H&WC, Health and Welfare Canada (1978). *Guidelines for Canadian Drinking Water Quality*, 1978, Supporting Documentation. pp. 645-676
- Janssens, J.G. (1990). Possibilities and Limitations of Oxidation and Disinfection Processes in Relation to Drinking Water Regulations. Presented at the Joint Annual Conference: Ontario Section AWWA and Ontario Municipal Water Association.
- Kreft, P., M. Umphres, J. Hand, C. Tate, M.J. McGuire and R.R. Trussell (1985). Converting From Chlorine to Chloramines: A Case Study. *JAWWA*, 77:1, 38-45.
- Kruithof, J.C. (1986). *Chlorination By-Products: Production and Control*. KWIA Communication No. 74. American Water Works Association Research Foundation.
- Larocque, R.L. (1990). Ozone for the Treatment of Drinking Water Supplies. *Environmental Science & Engineering*, 7, 38-40.
- Lauer, W.C., S.R. Lohman and S.E. Rogers (1986). Experience With Chlorine Dioxide at Denver's Reuse Plant. *JAWWA*, 78:6, 79-87.
- LePage, W.L. (1985). A Treatment Plant Operator Assesses Ozonation. *JAWWA*, 77:8, 44-48.

- Martin, G.W., G.G. Luck, and H.J. Graham (1985). *Trihalomethanes in Ontario Drinking Waters, A Survey of Selected Water Treatment Plants*. Ontario Ministry of the Environment.
- Orme, J. (1989). In: *Face to Face, Disinfection By-Products*. *JAWWA*, 81:8, 18-26.
- Orme, J. (1990). Potential Health Risks of Drinking Water Disinfection By-Products. *Disinfection By-Products, Current Perspectives*. American Water Works Association, Colorado. pp. 208-215.
- Orme, J., D.H. Taylor, R.D. Laurie and R.J. Bull (1985). Effects of Chlorine Dioxide on Thyroid Function in Neonatal Rats. *J. Toxicol. Environ. Health*. 15:2, 315-322.
- Orme, J., C.S. Mullin and E.V. Ohanian (1990). Health Effects of Disinfectants and Disinfection By-products: A Regulatory Perspective. In: *Water Chlorination: Chemistry, Environmental Impact and Health Effects, Volume 6.*, pp. 78-86. Lewis Publishers, Michigan.
- Prendiville, P.W. (1985). In: *Roundtable, Trends in Ozonation*. *JAWWA*, 77:8, 19-30.
- Ram, N.M., R.F. Christman and K.P. Cantor (1990). In: *Significance and Treatment of Volatile Organic Compounds in Water Supplies*. Lewis Publishers, Michigan.
- Reckhow, D.A., P.C. Singer and R.R. Trussell (1986). Ozone as a Coagulant Aid. In: *AWWA Seminar Proceedings. Ozonation: Recent Advances and Research Needs*. Annual Conference. June 22, 1986. Denver, Colorado. American Water Works Association, Denver, CO. pp. 17-46.
- Roberts, P.V. and Levy, J.A. (1985). Energy Requirements for Air Stripping Trihalomethanes. *JAWWA*, 77:4, 138-146.
- Rook, J.J. (1974). Formation of Haloforms during Chlorination of Natural Waters. *Water Treatment Exam.* 23:2, 234-243.

- Sayer, I.M. (1985). Chloramines: A Practical Alternative (Theme Introduction). *JAWWA*, 77:1, 33.
- Singer, P.C. (1989). Formation and Control of Trihalomethanes. *Disinfection By-Products, Current Perspectives*. American Water Works Association, Colorado. pp. 219-231.
- Singer, P.C. (1990). Assessing Ozonation Research Needs in Water Treatment. *JAWWA*, 82:10, 78-88.
- Symons, J.M., A.A. Stevens, R.M. Clark, E.E. Geldreich, O.T. Love Jr. and J. DeMarco (1981). *Treatment Techniques for Controlling Trihalomethanes in Drinking Water* (USEPA, 1981, American Water Works Association, 1982).
- Vajdic, A.V. (1982). *Alternative Disinfection Methods in Drinking Water Treatment*. Ontario Ministry of the Environment.
- Vajdic, A.V. (1983). *Carbon Filtration in Drinking Water Treatment*. Ontario Ministry of the Environment.
- Vajdic, A.V. (1989a). Trihalomethane Guideline - Further Issue. Personal communication. Unpublished.
- Vajdic, A.V. (1989b). Drinking Water Objectives, An Example of Federal-Provincial Co-operation. Presented at the Ontario Section AWWA 30th Water Works Seminar.
- White, G.C. (1986). *Handbook of Chlorination*. Van Nostrand Reinhold, New York.